

## Thermal Energy of Mixtures II

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We have found that conservation of Internal Energy, hence upholding the first law of thermodynamics, obliges us to include configurational entropy in Internal Energy.

We recall:

$$U = U_{\text{mic}} - TS_{\text{conf}} \quad (\text{generally } U = U_{\text{mic}} - \int dTS_{\text{conf}}(T))$$

$U_{\text{mic}}$  is the microscopic Internal Energy,  $S_{\text{conf}}$  is the configurational entropy of the mixture.  
Heat capacity becomes

$$C_V = C_{V\text{mic}} - S_{\text{conf}}$$

For pure substances,  $S_{\text{conf}} = 0$  and there is no contribution.

How come we got the right result in osmosis without this modification of Internal Energy?

In osmosis, the pressure difference is obtained by equating water chemical potential on each side of a semi-permeable membrane. If, however, we plug our new expression for Internal Energy in, we somehow "double up" the entropy effect arriving at a glaring contradiction.

The reason is that our original reasoning was wrong.

It is not chemical potential that has to be constant, it is Internal Energy that must not change upon the exchange of water particles from one side to the other

Consider the change of Internal Energy (incompressible fluid) including particle exchange

$$dU = TdS + \mu_j dN_j$$

We want

$$dU = 0$$

What we need is to take into account is the change of entropy during a particle exchange

$$dS = s_j dN_j$$

$s_j$  is the *molar* entropy of species  $j$ .

This term *exactly cancels* the entropy term contained in the chemical potential, leaving us with the requirement

$$\Delta u_j = v_j \Delta p$$

$u, v$  are molar quantities (internal energy, volume) of the transmitted species

Since we included configurational entropy into Internal Energy in the same way it was contained in chemical potential, we get the same result as the one previously derived by the "wrong" approach.

An experimental test of this hypothesis would be the measurement of specific heat as a function of configurational entropy, species concentration that is to say, under conditions excluding any parasitic effects. We have such conditions when mixing *isotopes* of one single species.

Practically, take molten metal of two isotopes and measure specific heat vs isotope proportion.

Choose isotopes of same nuclear spin to avoid quantum statistical issues.

We should get a minimum of specific heat at equal isotope content.

Now that we are done with the nitty-gritty, let us point out that in this year 2024AD, after 200 years of thermodynamics and 150 years of Boltzmann's definition of entropy, we have, on top of kinetic and interaction energy, discovered a new, third, form of energy - *configurational energy*.